Geiger, F., McNeill, F., & Orr-Ewing, A. J. (2020). Virtual Issue in Atmospheric Chemistry Research. *Journal of Physical Chemistry A*, *124*(28), 5697-5699. https://doi.org/10.1021/acs.jpca.0c05353

Virtual Issue in Atmospheric Chemistry Research

The *Journal of Physical Chemistry A* and *ACS Earth and Space Chemistry* both publish high quality articles at the forefront of research exploring the chemistry of the Earth's atmosphere. This Virtual Issue brings together examples of articles published in the two journals over the past 3 years to illustrate the breadth of topics in atmospheric chemistry that are of interest to their readership. The collection of papers it comprises may also serve as a helpful supplement to graduate or upper-level undergraduate class in atmospheric chemistry.

Progress with understanding the complex chemistry of the Earth's atmosphere requires synergy between different approaches. Field measurements at a range of locations determine the atmospheric composition of trace gases and particles, and they test the validity of computer model simulations designed to explore how chemical and physical processes affect this composition. In turn, the architecture of these models derives from laboratory and computational chemistry studies of chemical and physical mechanisms. The models draw their input parameters from laboratory determinations of thermodynamic, spectroscopic and reaction kinetic parameters for the constituent molecular species, as well as assessments of emissions from natural and anthropogenic sources. The research published in the *Journal of Physical Chemistry A* and *ACS Earth and Space Chemistry* contributes significantly to all these facets of atmospheric chemistry. It addresses the growing recognition, both within and beyond the scientific community, of the consequences of human activity for air quality and climate, with an emphasis on developing a molecular-level understanding of the various processes of interest.

Much of the chemistry of the lowest region of the atmosphere, the troposphere, is driven by sunlight and involves complex multi-step oxidation pathways of volatile organic compounds (VOCs). These VOCs are emitted from a variety of sources ranging from natural vegetation to human activities. Some of the VOC oxidation pathways produce oxygenated intermediates of lower volatility which can condense to form secondary organic aerosol (SOA) particles. Quantification of the impact of VOC emissions on the atmosphere must therefore integrate knowledge of the inter-connected photochemistry and chemical reactivity occurring in both gas- and condensed-phase environments. In addition to SOA, these latter environments include mineral particles, aqueous droplets, snowpack, and the surface waters of the oceans. The articles selected for this VI consider chemistry under a range of such conditions. Many focus on what happens at the interfaces between air and various aqueous environments. They examine topical scientific questions concerning the nucleation, growth, and photochemical processing of atmospheric particles. The research methods applied include a range of advanced spectroscopic and mass spectrometric techniques, as well as theoretical predictions of reaction pathways and rate coefficients based on quantum chemical calculations.

The complex oxidation processes of VOCs and their implications for SOA particle growth are considered in several articles highlighted in this Virtual Issue. The hydroxyl radical (OH) is known to initiate many of the daytime oxidation pathways for VOCs, but unravelling the complexity of these radical-mediated mechanisms for compounds such as biogenically emitted terpenes requires detailed laboratory investigations.[1] Ozone photolysis is the most significant source of tropospheric OH radicals, but elevated concentrations of HONO above snowpack, traced to the solar photochemistry of nitrate and nitrite ions in the snow, provides a significant alternative winter-time source of OH.[2] At night, other

oxidants take center stage; for example, the nitrate radical (NO_3) reacts with VOCs from both natural and industrial sources.[3] Both in the daytime and at night, ozone-initiated oxidation of unsaturated VOCs produces zwitterionic carbonyl oxide compounds commonly called Criegee intermediates which have attracted considerable recent attention. The unusual reactivity of these Criegee intermediates has been the subject of numerous laboratory studies, with a growing focus on the formation of lower volatility adducts which might contribute to SOA production in forested regions where biogenic emissions of terpenes are high.[4, 5] Autooxidation reactions of VOCs are also now recognized to lead to highly oxidized multifunctional compounds which condense into SOA, but nitrogen oxides have been shown to suppress this oxidation chemistry.[6]

Modern theoretical methods can accurately compute the rates and mechanisms of gas-phase reactions contributing to VOC oxidation pathways using a combination of quantum-chemical electronic structure calculations and reaction rate theories.[7-9] Thus, in combination with experimental investigations, these theoretical approaches are helping to unravel the atmospheric fates of VOCs. Further applications include prediction of the environmental impacts of proposed replacements for industrial gases with large ozone depletion and global warming potentials.[10] These quantum-chemistry techniques are also now being used to explore the mechanisms by which new particles form in the atmosphere by simulating the intermolecular interactions and reactions taking place in small molecular clusters.[11-13]

The complexity of the chemical and physical processes that occur in atmospheric aerosol is clearly illustrated by several of the articles selected for the Virtual Issue. Reactions of OH radicals, or of Criegee intermediates with surface-active organic compounds at the air-water interfaces of aqueous droplets are routes to greater molecular complexity in organic aerosols,[14, 15] as is direct solar photochemistry of organic compounds dissolved in these droplets.[16-18] Other trace atmospheric components including N_2O_5 will also oxidize solutes in aqueous droplets, but the resulting release of reactive gases such as $ClNO_2$ was recently shown to be inhibited by co-solutes such as sulfate and carboxylates.[19] The partitioning of gaseous organic compounds to the surfaces of aerosol particles affects their cross-sections for scattering and absorption of solar radiation,[20] with consequences for the direct effect of these aerosol particles on radiative forcing of the atmosphere. Mineral inclusions in aerosol droplets can catalyse the photochemical conversion of certain organic solutes to compounds such as organosulfates which contribute to the complexity of SOA composition.[21] Dissolved organic matter and surface-active organic compounds also modify the hygroscopicity and surface tension of the particles, and hence their propensity to act as cloud condensation nuclei.[22, 23] The coating of aqueous droplet surfaces by surfactant organic molecules inhibits dissolution of ambient gases including CO_2 with consequences for the droplet pH.[24] Microbe metabolism can change the organic composition of cloud and aerosol droplets, but the density of metabolically active cells in the atmosphere is low.[25] Sea spray aerosol is a complicated aqueous mixture of biological, organic and organic compounds, and as it dries in air will undergo crystallization or liquid-liquid phase separation.[26] Phase separation is also induced by freezing of aqueous droplets, leading to concentrated solutions around an ice core.[27] Interfacial chemistry of atmospheric importance is not limited to aerosol droplets: the significance of the photochemistry of semi-volatile organic compounds deposited in films on the many surfaces present in urban environments is now being recognized.[28] For example, these coatings enhance the dry deposition of dispersed particulate matter.

The concentrations and properties of particulate matter (PM) impact air quality and climate and are affected by both natural and anthropogenic events. Large field studies of wildfires in the western USA

have provided an opportunity in recent years to study both the emission and photochemical processing of sub-micron aerosol particles and the mechanisms leading to their changing chemical composition.[29] The devastation caused by Hurricane Maria in 2017 included extensive damage to the electrical grid in Puerto Rico. As a consequence, increasing use of backup generators raised levels of air pollution in San Juan at the same time that power loss disabled local air pollution monitors, necessitating intervention with lower-cost solar-powered sensors.[30] Analysis of the organic content of PM in southern China showed the presence of compounds deleterious to health from sources including crop burning, providing insights for air pollution mitigation in that area.[31]

Higher in the atmosphere, the chemistry of the mesosphere is influenced less by emissions from the planet's surface and more by materials originating from space. For example, ablation of meteorites releases reactive metals with complex chemistries that are amenable to resolution by the same combined strategies of laboratory measurements and theoretical predictions.[32] However, the chemistry of the upper atmosphere remains less well-studied than that of the troposphere, in part because of a relative paucity of measurements of the chemical composition. Driven by greater availability of observational and in situ measurement data, studies of the chemistry of the atmospheres of other planets in the solar system and of exoplanets are also expected to be expanding fields of future activity well suited to publication in our two journals.

The *Journal of Physical Chemistry A* and *ACS Earth and Space Chemistry* provide highly respected platforms with wide reach for the dissemination of research in all areas of atmospheric chemistry. The editors look forward to supporting the publication of further ground-breaking studies across all areas of this topical field of research.

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

Franz M. Geiger, Senior Editor, the Journal of Physical Chemistry, and Northwestern University ORCID: 0000-0001-8569-4045

V. Faye McNeill, Associate Editor, ACS Earth and Space Chemistry, and Columbia University. ORCID: 0000-0003-0379-6916

Andrew J. Orr-Ewing, Senior Editor, the Journal of Physical Chemistry and University of Bristol, ORCID: 0000-0001-5551-9609

References

1. Xu, L.; Møller, K. H.; Crounse, J. D.; Otkjær, R. V.; Kjaergaard, H. G.; Wennberg, P. O., Unimolecular Reactions of Peroxy Radicals Formed in the Oxidation of α-Pinene and β-Pinene by Hydroxyl Radicals. *The Journal of Physical Chemistry A* **2019,** *123*, 1661-1674.
2. Chen, Q.; Edebeli, J.; McNamara, S. M.; Kulju, K. D.; May, N. W.; Bertman, S. B.; Thanekar, S.; Fuentes, J. D.; Pratt, K. A., HONO, Particulate Nitrite, and Snow Nitrite at a Midlatitude Urban Site during Wintertime. *ACS Earth and Space Chemistry* **2019,** *3*, 811-822.
3. Zhou, L.; Ravishankara, A. R.; Brown, S. S.; Idir, M.; Zarzana, K. J.; Daële, V.; Mellouki, A., Kinetics of the Reactions of NO3 Radical with Methacrylate Esters. *The Journal of Physical Chemistry A* **2017,** *121*, 4464-4474.
4. Tadayon, S. V.; Foreman, E. S.; Murray, C., Kinetics of the Reactions between the Criegee Intermediate CH2OO and Alcohols. *The Journal of Physical Chemistry A* **2018,** *122*, 258-268.
5. Chhantyal-Pun, R.; Rotavera, B.; McGillen, M. R.; Khan, M. A. H.; Eskola, A. J.; Caravan, R. L.; Blacker, L.; Tew, D. P.; Osborn, D. L.; Percival, C. J.; Taatjes, C. A.; Shallcross, D. E.; Orr-Ewing, A. J., Criegee Intermediate Reactions with Carboxylic Acids: A Potential Source of Secondary Organic Aerosol in the Atmosphere. *ACS Earth and Space Chemistry* **2018,** *2*, 833-842.
6. Rissanen, M. P., NO2 Suppression of Autoxidation–Inhibition of Gas-Phase Highly Oxidized Dimer Product Formation. *ACS Earth and Space Chemistry* **2018,** *2*, 1211-1219.
7. Kuwata, K. T.; Luu, L.; Weberg, A. B.; Huang, K.; Parsons, A. J.; Peebles, L. A.; Rackstraw, N. B.; Kim, M. J., Quantum Chemical and Statistical Rate Theory Studies of the Vinyl Hydroperoxides Formed in trans-2-Butene and 2,3-Dimethyl-2-butene Ozonolysis. *The Journal of Physical Chemistry A* **2018,** *122*, 2485-2502.
8. Møller, K. H.; Bates, K. H.; Kjaergaard, H. G., The Importance of Peroxy Radical Hydrogen-Shift Reactions in Atmospheric Isoprene Oxidation. *The Journal of Physical Chemistry A* **2019,** *123*, 920-932.
9. Zhao, X.; Wang, L., Atmospheric Oxidation Mechanism of Furfural Initiated by Hydroxyl Radicals. *The Journal of Physical Chemistry A* **2017,** *121*, 3247-3253.
10. Rao, P. K.; Gejji, S. P., Kinetics and Mechanistic Investigations of Atmospheric Oxidation of HFO-1345fz by OH Radical: Insights from Theory. *The Journal of Physical Chemistry A* **2017,** *121*, 595-607.
11. Elm, J.; Passananti, M.; Kurtén, T.; Vehkamäki, H., Diamines Can Initiate New Particle Formation in the Atmosphere. *The Journal of Physical Chemistry A* **2017,** *121*, 6155-6164.
12. Wang, C.-Y.; Jiang, S.; Liu, Y.-R.; Wen, H.; Wang, Z.-Q.; Han, Y.-J.; Huang, T.; Huang, W., Synergistic Effect of Ammonia and Methylamine on Nucleation in the Earth's Atmosphere. A Theoretical Study. *The Journal of Physical Chemistry A* **2018,** *122*, 3470-3479.
13. Xu, J.; Finlayson-Pitts, B. J.; Gerber, R. B., Proton Transfer in Mixed Clusters of Methanesulfonic Acid, Methylamine, and Oxalic Acid: Implications for Atmospheric Particle Formation. *The Journal of Physical Chemistry A* **2017,** *121*, 2377-2385.
14. Enami, S.; Colussi, A. J., Reactions of Criegee Intermediates with Alcohols at Air–Aqueous Interfaces. *The Journal of Physical Chemistry A* **2017,** *121*, 5175-5182.
15. Huang, Y.; Barraza, K. M.; Kenseth, C. M.; Zhao, R.; Wang, C.; Beauchamp, J. L.; Seinfeld, J. H., Probing the OH Oxidation of Pinonic Acid at the Air–Water Interface Using Field-Induced Droplet Ionization Mass Spectrometry (FIDI-MS). *The Journal of Physical Chemistry A* **2018,** *122*, 6445-6456.
16. Eugene, A. J.; Guzman, M. I., Reactivity of Ketyl and Acetyl Radicals from Direct Solar Actinic Photolysis of Aqueous Pyruvic Acid. *The Journal of Physical Chemistry A* **2017,** *121*, 2924-2935.
17. Reed Harris, A. E.; Pajunoja, A.; Cazaunau, M.; Gratien, A.; Pangui, E.; Monod, A.; Griffith, E. C.; Virtanen, A.; Doussin, J.-F.; Vaida, V., Multiphase Photochemistry of Pyruvic Acid under Atmospheric Conditions. *The Journal of Physical Chemistry A* **2017,** *121*, 3327-3339.

18. Walhout, E. Q.; Yu, H.; Thrasher, C.; Shusterman, J. M.; O'Brien, R. E., Effects of Photolysis on the Chemical and Optical Properties of Secondary Organic Material Over Extended Time Scales. *ACS Earth and Space Chemistry* **2019,** *3*, 1226-1236.
19. Staudt, S.; Gord, J. R.; Karimova, N. V.; McDuffie, E. E.; Brown, S. S.; Gerber, R. B.; Nathanson, G. M.; Bertram, T. H., Sulfate and Carboxylate Suppress the Formation of ClNO2 at Atmospheric Interfaces. *ACS Earth and Space Chemistry* **2019,** *3*, 1987-1997.
20. Li, K.; Li, J.; Wang, W.; Li, J.; Peng, C.; Wang, D.; Ge, M., Effects of Gas-Particle Partitioning on Refractive Index and Chemical Composition of m-Xylene Secondary Organic Aerosol. *The Journal of Physical Chemistry A* **2018,** *122*, 3250-3260.
21. Schmidt, M.; Jansen van Beek, S. M.; Abou-Ghanem, M.; Oliynyk, A. O.; Locock, A. J.; Styler, S. A., Production of Atmospheric Organosulfates via Mineral-Mediated Photochemistry. *ACS Earth and Space Chemistry* **2019,** *3*, 424-431.
22. Barati, F.; Yao, Q.; Asa-Awuku, A. A., Insight into the Role of Water-Soluble Organic Solvents for the Cloud Condensation Nuclei Activation of Cholesterol. *ACS Earth and Space Chemistry* **2019,** *3*, 1697-1705.
23. Bé, A. G.; Chase, H. M.; Liu, Y.; Upshur, M. A.; Zhang, Y.; Tuladhar, A.; Chase, Z. A.; Bellcross, A. D.; Wang, H.-F.; Wang, Z.; Batista, V. S.; Martin, S. T.; Thomson, R. J.; Geiger, F. M., Atmospheric β-Caryophyllene-Derived Ozonolysis Products at Interfaces. *ACS Earth and Space Chemistry* **2019,** *3*, 158-169.
24. Cohen, L.; Quant, M. I.; Donaldson, D. J., Real-Time Measurements of pH Changes in Single, Acoustically Levitated Droplets Due to Atmospheric Multiphase Chemistry. *ACS Earth and Space Chemistry* **2020**.
25. Fankhauser, A. M.; Antonio, D. D.; Krell, A.; Alston, S. J.; Banta, S.; McNeill, V. F., Constraining the Impact of Bacteria on the Aqueous Atmospheric Chemistry of Small Organic Compounds. *ACS Earth and Space Chemistry* **2019,** *3*, 1485-1491.
26. Nandy, L.; Liu, S.; Gunsbury, C.; Wang, X.; Pendergraft, M. A.; Prather, K. A.; Dutcher, C. S., Multistep Phase Transitions in Sea Surface Microlayer Droplets and Aerosol Mimics using Microfluidic Wells. *ACS Earth and Space Chemistry* **2019,** *3*, 1260-1267.
27. Bogdan, A.; Molina, M. J., Physical Chemistry of the Freezing Process of Atmospheric Aqueous Drops. *The Journal of Physical Chemistry A* **2017,** *121*, 3109-3116.
28. Styler, S. A.; Baergen, A. M.; Donaldson, D. J.; Herrmann, H., Organic Composition, Chemistry, and Photochemistry of Urban Film in Leipzig, Germany. *ACS Earth and Space Chemistry* **2018,** *2*, 935-945.
29. Garofalo, L. A.; Pothier, M. A.; Levin, E. J. T.; Campos, T.; Kreidenweis, S. M.; Farmer, D. K., Emission and Evolution of Submicron Organic Aerosol in Smoke from Wildfires in the Western United States. *ACS Earth and Space Chemistry* **2019,** *3*, 1237-1247.
30. Subramanian, R.; Ellis, A.; Torres-Delgado, E.; Tanzer, R.; Malings, C.; Rivera, F.; Morales, M.; Baumgardner, D.; Presto, A.; Mayol-Bracero, O. L., Air Quality in Puerto Rico in the Aftermath of Hurricane Maria: A Case Study on the Use of Lower Cost Air Quality Monitors. *ACS Earth and Space Chemistry* **2018,** *2*, 1179-1186.
31. He, X.; Huang, X. H. H.; Chow, K. S.; Wang, Q.; Zhang, T.; Wu, D.; Yu, J. Z., Abundance and Sources of Phthalic Acids, Benzene-Tricarboxylic Acids, and Phenolic Acids in PM2.5 at Urban and Suburban Sites in Southern China. *ACS Earth and Space Chemistry* **2018,** *2*, 147-158.
32. Mangan, T. P.; McAdam, N.; Daly, S. M.; Plane, J. M. C., Kinetic Study of Ni and NiO Reactions Pertinent to the Earth's Upper Atmosphere. *The Journal of Physical Chemistry A* **2019,** *123*, 601-610.